



# CIEEMAT`19

The 5th Ibero-American Congress on  
Entrepreneurship, Energy, Environment  
and Technology

## PROCEEDINGS



# Use of leachates from a mechanical biological municipal solid waste treatment plant as fertilizers

Jonathan Cardoso, Maria Vertonha, Juliana Mees, Jose Luis Díaz Tuesta, Paulo Brito, Helder T. Gomes

Jonathan Cardoso  
*Centro de Investigação de Montanha (CIMO)/Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM)*  
 Instituto Politécnico de Bragança/  
 Universidade do Porto  
 Bragança, Portugal  
 jonahancardoso@ipb.pt

Maria T. Vertonha  
*Centro de Investigação de Montanha (CIMO)*  
 Instituto Politécnico de Bragança  
 Bragança, Portugal  
 mvertonha@gmail.com

Juliana B. Mees  
*Programa de Pós-Graduação em Tecnologias Ambientais*  
 Universidade Tecnológica Federal do Paraná, Campus de Medianeira  
 Paraná, Brasil  
 juliana@utfpr.edu.br

Jose Luis Díaz de Tuesta  
*Centro de Investigação de Montanha (CIMO)/Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM)*  
 Instituto Politécnico de Bragança/  
 Universidade do Porto  
 Bragança, Portugal  
 jl.diazdetuesta@ipb.pt

Paulo Brito  
*Centro de Investigação de Montanha (CIMO)*  
 Instituto Politécnico de Bragança  
 Bragança, Portugal  
 paulo@ipb.pt

Helder T. Gomes  
*Centro de Investigação de Montanha (CIMO)/Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials (LSRE-LCM)*  
 Instituto Politécnico de Bragança/  
 Universidade do Porto  
 Bragança, Portugal  
 htgomes@ipb.pt

**Abstract**— Leachate liquid streams originated from treatment plants contain carbon, nitrogen, phosphorus, potassium and trace elements. The present work aims to assess if a leachate, generated from a composting line of a mechanical and biological treatment facility, can be used as a potential source for liquid fertilizers, and thus propose and design a sequence of processes which could effectively convert the leachates to commercial liquid fertilizers according to the requirements of the proposal of regulation of the European Parliament of 2016 [1], [2]. The analysis shows that the leachate exhibits potential to be converted in an organo-mineral fertilizer, since it exhibits high organic carbon content. However, some heavy metals and nitrogen and phosphorus nutrient contents do not fulfill the legislation requirements which implies a tuning of the liquid waste composition.

**Keywords**— Treatment plant, leachate, waste processes, fertilizers.

## I. INTRODUCTION

Each year an increasing quantity of wastes is disposed in the nature, which not only causes economic and environmental problems for the society, but also represents a waste of resources. The generation of wastes in Europe has raised in 21 of the 31 Member States for municipal waste generated per capita since 1995. Specifically, in Portugal, the rate of wastes generation increased 34.7%. The variations reflect differences in consumption patterns and economic wealth, but also depend on how municipal waste is collected and managed [3]. The management of deposition of organic fractions of municipal solid waste on landfill, and new treatments and applications to the subsequent leachates must be developed. Several successful demonstrations of leachate application by irrigation of crops were reported in different parts around Europe [1], [4], [5].

Leachate is an obvious waste product without associated direct production costs. However, it usually implies a previous expensive treatment process before it can be discarded. The possibility of using leachates in agriculture applications also means that the costs at waste treatment plants can be reduced,

since the removal of nitrogen, phosphorus and other useful substances would not be necessary. Nevertheless, due to the nature of the leachates, they may contain, in addition to elements of interest, heavy metals, phytotoxic substances such as ammonia, organic compounds of low molecular weight and high salt content [6]–[8]. The aim of this work is the proposal and design of a sequence of processes to convert a specific leachate liquid stream with a highly variable composition, collected from the composting line of a mechanical and biological treatment facility, into commercial fertilizers which fit the composition requirements of the European Legislation. But, to effectively design these processes, it is necessary to assess the typical composition of the liquid leachate and to predict its possible variability, for the evaluation of the composition alteration needs. Therefore, in the present work the data gathered for the characterization of the leachate is presented and discussed, and a conversion sequence of processes is proposed.

## II. MATERIALS AND METHODS

The samples were obtained from the leachate storage tank from a composting line of a mechanical and biological treatment plant of organic wastes at the company Resíduos do Nordeste, EIM (Mirandela, Portugal). The samples were collected in June 2018 and February 2019, and then were stored at 4°C in 5 L PET bottles. The concentration procedure was performed using simple distillation. The ratio between the initial and final volume is given as the concentration factor which is used for the identification of each sample. pH and conductivity were determined using a pH electrode SenTix 41 and a conductivity cell TetraCon 325.

TOC analysis was performed with 1:500 dilution, in a Shimadzu TOC-L equipment. Density assessment was done using Anton Paar DMA5000M densimeter at 20°C. Dry mass percentage was obtained using an oven from Scientific Series 9000 at 105°C for 48 h while Ash percentage was performed at 450°C until constant mass. Heavy metals quantification was performed by digesting the samples with HNO<sub>3</sub>/HCl during 48 h at 6°C, filtrated using a 0.45 µm syringe filter in a 50 mL

volumetric flask and analysis by atomic absorption spectroscopy Varian SpectrAA 220.

Ammoniacal Nitrogen was characterized through distillation of the initial sample. Total Kjeldhal Nitrogen (TKN) analysis was performed using the same procedure with previous digestion with  $H_2SO_4$ . Organic Nitrogen was calculated through the difference between Total and Ammoniacal Nitrogen. Phosphorous analysis was performed by digesting the sample with  $HNO_3$  and  $HClO_4$ , and the absorbance measurements were carried out in a Jasco UV/VIS spectrophotometer at 400 nm, using vanadate molybdate solutions as colorants.

Nitrite was characterized using dilutions of the initial sample from 1:50 to 1:400 in a 50 mL volumetric flask. In each flask, 1 ml of sulfanilamide solution was added. The absorbance measurements were carried out in a Jasco UV/VIS spectrophotometer at 537 nm. Nitrate was characterized using dilutions of the initial sample from 1:50 to 1:400 in a 50 mL volumetric flask. In each flask, 1 ml of HCl 1 M was added. The absorbance measurements were carried out in a Jasco UV/VIS spectrophotometer at 220 nm and 275 nm to eliminate the organic matter effect. The final absorbance is obtained as following in Equation 1.

$$A_{Real} = A_{220} - (2 \times A_{275}) \quad (1)$$

The adsorbent materials were activated carbon samples produced from the compost material generated in the treatment plant and acid activated clays obtained in a partnership with a Kazakhstan institution.

The activated carbon samples were produced from the compost provided by Resíduos do Nordeste, EIM, which was washed with distilled water, dried for 12h at 110°C, powdered and sifted, for homogenization. Different amounts of the compost were mixed with 30 mL of distilled water to obtain different initial concentrations and heated to targeted temperature as presented in Table I. Then, the solids were separated by vacuum filtration (pore size 0.45  $\mu m$ ), washed and dried for 15h at 100°C [9].

TABLE I. COMPOSITION AND TREATMENTS USED FOR THE ACTIVATED CARBON PRODUCED FROM THE COMPOST.

Sample	Reaction time (h)	Compost mass (g)	Reaction temperature (°C)
AC 10	4	3.00908	230
AC 11	2	3.00037	230
AC 12	2	2.00591	150

The natural clays, obtained from 4 different locations at Kazakhstan and identified as ASA, KAA, AKA and KOA, were purified with a mixture of sodium acetate and acetic acid. Acid activated clays samples were prepared by adding 3 g of the natural clay into a 250 mL three necked round bottom flask, and 150 mL of 4 M solution of  $H_2SO_4$ . The resulting suspension was stirred at 80°C during 3 h. The supernatant was discharged, and the activated clay was repeatedly washed until neutral pH. The activated clay was recovered and then dried in air static oven at 60°C overnight [10].

10mL of the leachate for the activated carbon and 20mL for the clays are mixed with 0.1g or 0.2g of each one of the solid adsorbent's samples for 48 hours at room temperature, centrifuged at 9000rpm and the supernatant is reserved at 4°C. The samples were characterized using TOC analysis,

performed with 1:500 dilution, in a Shimadzu TOC-L equipment. Heavy metals quantification was performed by digesting the samples with  $HNO_3/HCl$  during 48 h at 60°C, then filtrated using a 0.45  $\mu m$  syringe filter in a 50 mL volumetric flask, completed with a 5%  $HNO_3$  solution, and afterwards analyzed by atomic absorption spectroscopy using a Varian SpectrAA 220 apparatus.

### III. RESULTS AND DISCUSSION

Chemical properties of original and concentrated leachates are summarized in Table II for samples collected in June 2018 and February 2019, respectively, from the compost leachate storage facility.

TABLE II. CHEMICAL PROPERTIES OF ORIGINAL AND CONCENTRATED LEACHATES.

Samples	% TOC	pH	Density [g/cm <sup>3</sup> ]	Dry Mass [%w/w]	Ash [%w/w]	
EU 2016	3.00	-	-	<60	-	
Jun 2018	Original	1.22	7.95	1.01	2.76	1.36
	3.19x	3.64	6.43	1.04	8.26	4.31
	3.23x	3.63	6.44	1.04	8.21	4.23
	3.33x	3.46	6.40	1.04	8.58	4.39
	4.23x	4.65	6.48	1.06	11.19	5.64
	4.39x	4.63	6.49	1.06	11.26	5.81
Feb 2019	Original	2.81	7.53	1.03	6.49	3.07
	Original Filtered	2.79	7.81	1.03	6.02	2.96
	1.19x	3.27	7.98	1.04	7.03	2.93
	1.85x	5.36	6.55	1.06	11.43	5.59

The original leachate obtained at February 2019 showed a TOC concentration 2 times greater than the leachate samples collected at June 2018, which makes apparent the high heterogeneity of the leachate produced. Both original leachate samples must be concentrated to satisfy the requirements of the EU fertilizers legislation in order to reach 3% of TOC for liquid organo-mineral fertilizers [1], [2], [7], [8].

pH and density shown low variation between the original and the concentrated samples, remaining neutral with water removal. The original sample showed a higher content of dry mass and ashes compared to the original sample from June 2018. However, it is visible that the original sample from February 2019 needs less water removal to reach the target specifications.

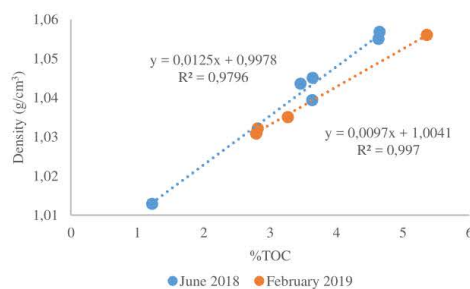


Fig. 1. Correlation between Density and TOC.

It is detected that the organic carbon content has a strong influence on the final density of the concentrate obtained.

Thus, some statistical analysis can now be applied to verify the possible correlation between bulk density and TOC for samples from June 2018 and February 2019, as shown in Fig. 1, which presents how density is affected by the TOC in each sample.

A significance test using Pearson's correlation coefficient was carried out. A Pearson correlation coefficient  $r = 0.99$  was obtained for both samples. Thus, it can be stated that the correlation between density and TOC values is statistically significant for a 99% confidence interval.

Heavy metals content was determined for all samples in order to verify the fulfillment of the EU legislation for organo-mineral liquid fertilizers. The results are presented in Table III.

TABLE III. HEAVY METALS CONTENT OF ORIGINAL AND CONCENTRATED LEACHATES.

Samples	Zn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cr (mg/kg)	
EU 2016	1500	600	3	120	50	2	
Jun 2018	3.19x	-	4.69	8.71	133.71	15.16	
	3.23x	-	1.84	8.73	153.26	11.48	
	3.33x	-	1.01	2.17	89.62	10.76	
	4.23x	-	4.79	12.13	134.92	15.58	
	4.39x	-	2.98	8.73	111.00	11.21	
Feb 2019	Original	468.60	101.60	0.37	4.76	116.33	10.74
	Original Filtered	252.78	241.15	0.91	4.11	148.93	9.83
	1.19x	1077.56	56.07	0.69	15.77	155.51	11.08
	1.85x	1299.82	11.27	0.41	11.10	62.81	10.47

For the heavy metals analysis is evident that the more suitable leachate for this application is the collected in February 2019, it shows a higher concentration of TOC with lower heavy metals content. The concentration of each heavy metal is highly variable mainly due to the significant heterogeneity of the leachate samples and the visible differences in the compositions of its liquid and solid fractions. However, it is noticeable that the content of Zn, Cu, Cd and Pb fulfill the requirements of the EU legislation in concentrated samples, while Ni and Cr must be removed to achieve EU requirements.

The characterization of nitrogen and phosphorous (NP) species was carried out to obtain the parameters for the leachate as shown in Table IV.

TABLE IV. NP CONTENT.

Sample	TKN (%w/w)	Organic N (%w/w)	P <sub>2</sub> O <sub>5</sub> (%w/w)
EU 2016	2	0.5	2
Jun 2018	0.0588	0.0453	<0.02
Feb 2019	0.3391	0.2617	<0.02

The original leachate obtained at February 2019 showed a nitrogen concentration 20 times greater than the leachate obtained in June 2018. The values obtained for total phosphorus are below the detection limit for the analysis even in more concentrated samples. According to European Union legislation, a liquid organo-mineral fertilizer must contain at least one of the following declared nutrients in the minimum quantities: 2%w/w of total N, of which 0.5%w/w must be organic nitrogen; 2%w/w of total P<sub>2</sub>O<sub>5</sub>; and 2%w/w of total K<sub>2</sub>O. Therefore, the nitrogen and phosphorous values do not fit the requirements in the legislation; it is necessary to carry

out the potassium analyses to verify possible conformances in at least one of the required nutrients.

The nitrite and nitrate content in the original filtered leachate are presented in Table V.

TABLE V. NITRITE AND NITRATE CONTENT.

Sample	Nitrite (mg/L)	Nitrate (mg/L)
Feb 2019	33.46	150.86

The nitrite and nitrate content are not a legislation demand. However, in comparison, this value is lower than the maximum requirements for other fertilizers.

From the analysis of original and concentrated leachate samples, a simplified flowsheet for a sequence of composition adjustments for the leachate can now be proposed, as presented in Fig. 2.

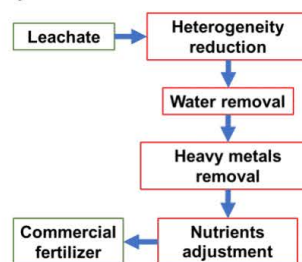


Fig. 2. Proposed simplified flowsheet for a conversion process of the leachate to commercial fertilizers.

This flowsheet represents a proposal for the main general operations that the leachate must pass through to reach the minimum legislation requirements for commercial fertilizers. The specific processes for each conversion step must be selected and designed, considering the predictable composition of the liquid leachate and its possible variation.

Tests using solid adsorbents such as activated carbon produced from the compost and acid activated clays are proposed to reduce the heavy metals content with minimum impact in the organic carbon concentration in the Original Filtered samples. Solid adsorbents are more suitable for an easier separation process.

Each treated leachate sample is identified by the adsorption solid used. For the activated carbon (AC) the treated leachate is coded by the name of the solid (10, 11 or 12), while for the activated clays the treated leachate is identified by the name of the solid from the four different regions of Kazakhstan: Akzhar (AKA), Asa (ASA), Karatau (KAA) and Kokshetau (KOA). Additionally, each test is also identified by the mass of adsorbent added to each leachate, 0.1 (0.1 g) or 0.2 (0.2 g). Total Organic Carbon (TOC) and heavy metals content of treated leachates are presented in Fig. 3, 4 and 5 for samples collected in February 2019 from the compost leachate storage facility according to the classification adopted following the legislation for organo-mineral fertilizers presented by the European Parliament [1], [2].

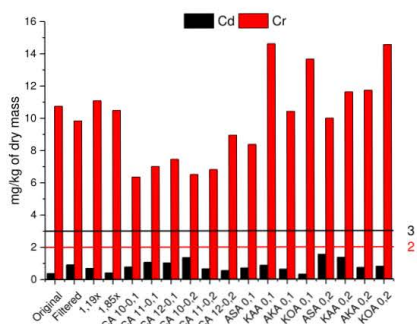


Fig. 3. Cd and Cr content.

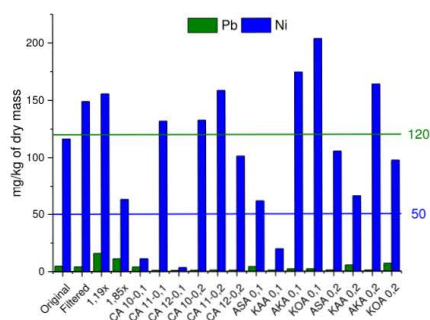


Fig. 4. Pb and Ni content.

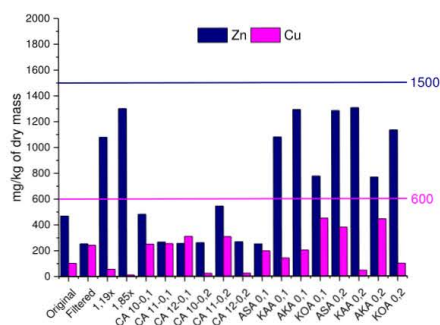


Fig. 5. Zn and Cu content.

The original leachate obtained at February 2019 presents an organic carbon content lower than the requirements of the EU fertilizers legislation (3% of TOC) for liquid organo-mineral fertilizers

The adsorption processes were tested using the filtered leachate samples in order to remove the effect of the suspended solids and ensure a better separation between phases after the adsorption process.

The adsorption materials showed interactions with the organic carbon present in the leachate, which promoted noticeable and undesirable removal of this carbon material from the liquid phase. The activated carbon promoted greater TOC removal in comparison with the activated clays, which could affect the heavy metals removal since it is possible that the organic carbon would occupy the adsorption centers blocking the suppression of heavy metals. The adsorption materials exhibited interaction with the heavy metals present in the leachates, with the leachate heterogeneity affecting greatly the results. Nevertheless Zn, Cu, Cd and Pb contents always satisfy the requirements. On the other hand, Ni and Cr still present higher content than the minimum allowed in the legislation. The samples treated with activated carbons produced from compost show lower heavy metals content.

#### IV. CONCLUSION

The concentrated leachate is not suitable, at this point, to be used as a commercial fertilizer, because it does not fit the totality of the legislation requirements. However, this processed waste leachate samples still display potential to be used for this type of applications, since it exhibits high concentrations of total organic carbon (TOC). Heavy metals content must be tubed, possibly resorting to adsorption materials. Nutrients like nitrogen and phosphorous are present in low levels even after the concentration procedure. Therefore, ultrafiltration or reverse osmosis processes are possible viable solutions to remove the excess of water without affecting significantly the content of the product in desirable compounds, especially nutrients and organic carbon. Potassium determination remains to be carried out and if it fits the legislation specification. However, the potential use of these leachate wastes as fertilizers is substantial, especially because it encourages the use of liquid wastes with high organic carbon content for agricultural applications with the possibility of producing a high value-added material.

Overall the activated carbons produced from the compost showed better results in heavy metals removal. However, while the adsorption materials promoted a reduction in the heavy metals content in most cases, this reduction also affected the organic carbon content, which is not an intended effect since it affects negatively the fulfillment of the TOC requirements. Nevertheless, ion-exchange resins will be now tested for a more efficient heavy metals removal in order to minimize possible secondary elimination of useful components such as organic carbon or nutrients.

#### ACKNOWLEDGMENT

This work was financially supported by: Project VALORCOMP, funded by FEDER through Programme INTERREG V-A Spain-Portugal (POCTEP) 2014-2020 and Associate Laboratory LSRE-LCM-UID/EQU/50020/2019-funded by national funds through FCT/MCTES (PIDDAC).

#### REFERENCES

- [1] European Comission, *European Parliament and European Council Proposal for the Regulation of fertilizers products with the CE marking and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009*. 2016.
- [2] European Comission, "Regulation of fertilizers products with the CE marking and amending 2016/0084.", 2019.
- [3] Eurostat, "Eurostat - Municipal waste statistics," no. July 2018, pp. 1-7, 2018.
- [4] K. Hyde, A. Smith, M. Smith, and S. Henningsson, "The challenge of waste minimisation in the food and drink industry: a

- demonstration project in East Anglia, UK," *J. Clean. Prod.*, vol. 9, pp. 57–64, 2001.
- [5] S. Henningsson, K. Hyde, A. Smith, and M. Campbell, "The value of resource efficiency in the food industry: a waste minimisation project in East Anglia, UK," *J. Clean. Prod.*, vol. 12, pp. 505–512, 2004.
- [6] T. Zhang, L. Ding, and H. Ren, "Pretreatment of ammonium removal from landfill leachate by chemical precipitation," vol. 166, pp. 911–915, 2009.
- [7] Ministério da Economia de Portugal, *Ministério da economia - Decreto-Lei n.º 103/2015*. 2015, pp. 3756–3788.
- [8] J. Cardoso, H. Gomes, and P. Brito, "Viability of the Use of Leachates from a Mechanical Biological Municipal Solid Waste Treatment Plant as Fertilizers," *Recycling*, vol. 4, no. 1, p. 8, 2019.
- [9] F. F. Roman, J. L. D. De Tuesta, P. Praça, A. M. T. Silva, J. L. Faria, and H. T. Gomes, "Production of low-cost hydrochars by hydrothermal carbonization of compost: kinetic modeling and treatment of the generated liquid effluent by Fenton," accepted for publication in 5th International Conference WASTES: Solutions, Treatments and Opportunities, Lisbon, Portugal, pp. 6–8, 2019.
- [10] A. S. Silva, "Treatment of wastewater containing pharmaceutical compounds by catalytic wet peroxide oxidation using clay-based materials as catalysts," MSc. Thesis, Polytechnic Institute of Bragança, 2019.